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(54) Hydride Container

(57) A gas containment system comprises a pressure vessel 60 in which gas absorbing solid particles are located in a plurality of closed containers as 20 in Figure 1 permeable to the gas. The system is particularly suitable for the storage of hydrogen on hydridable metals.

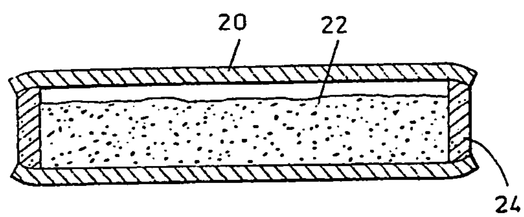
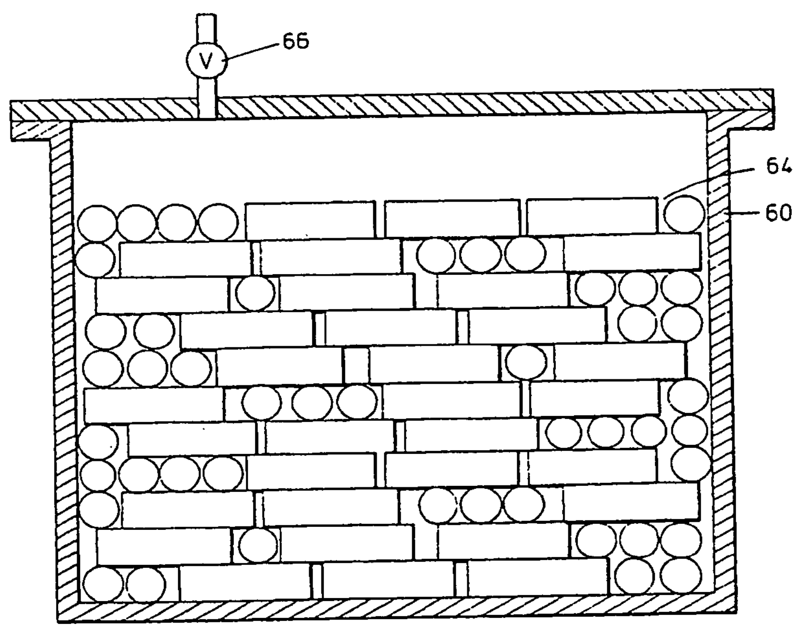


FIG. 1.

FIG. 5.



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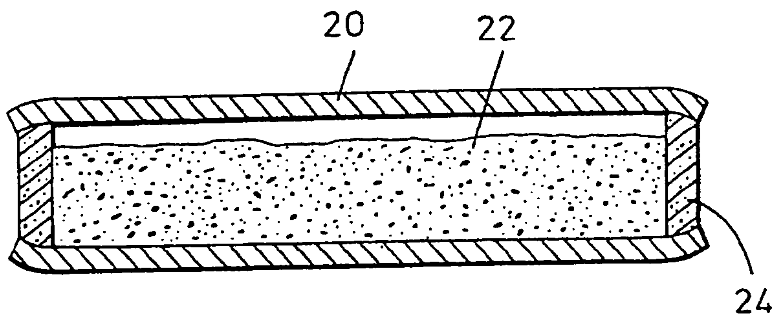
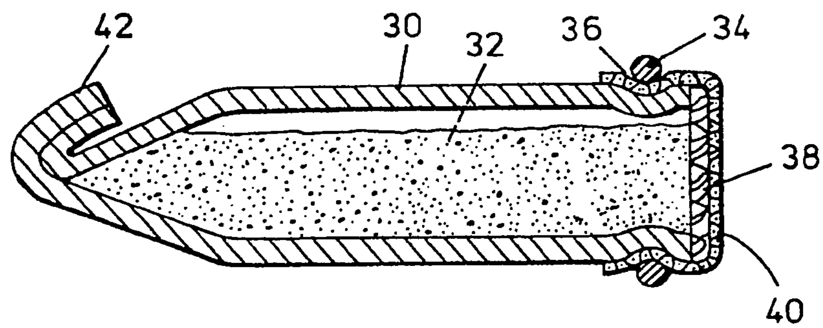


FIG.1.

FIG.2.



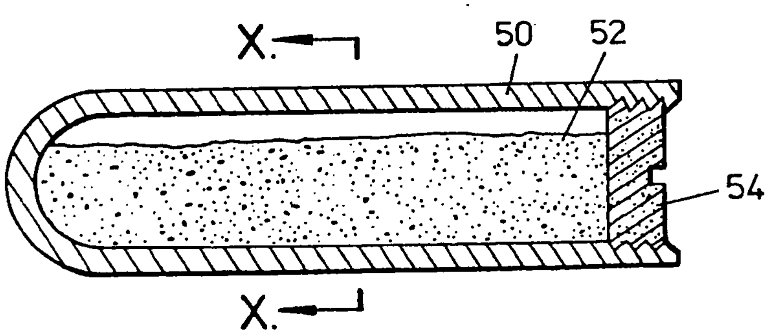


FIG.3.

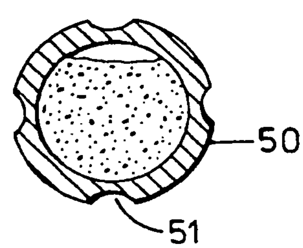
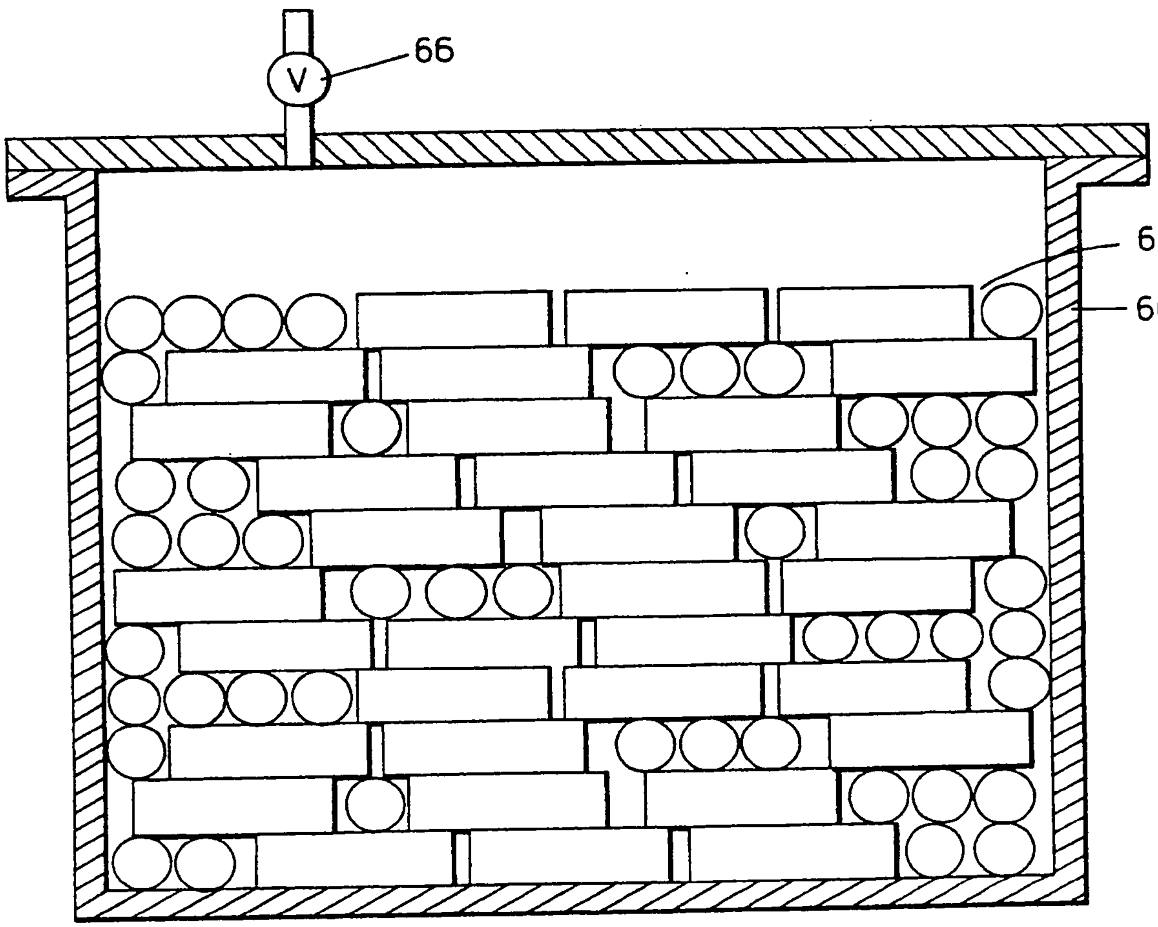


FIG.4.

FIG.5.



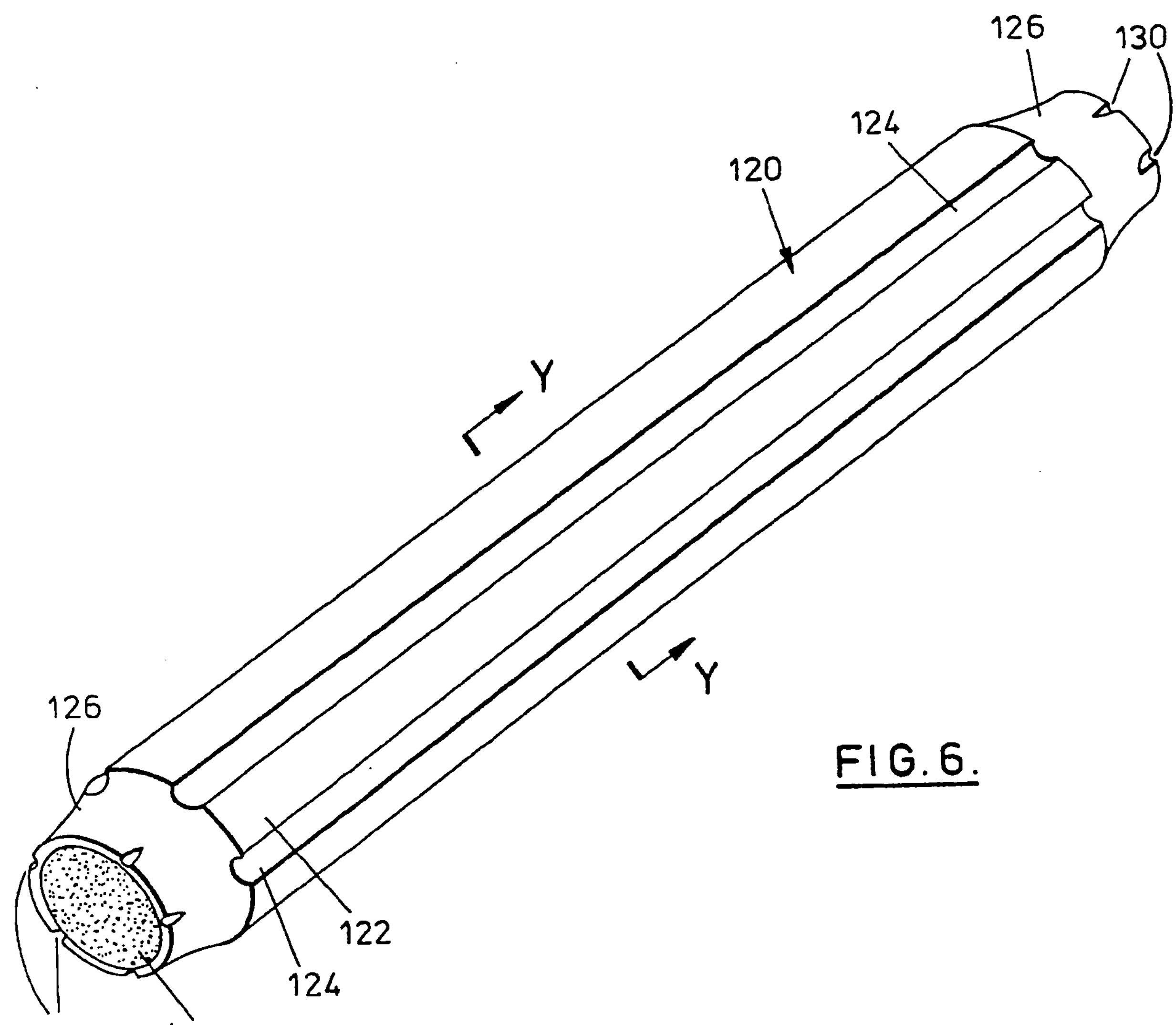

126
130
124
120
Y
Y
126
122
124
130
128

FIG. 6.

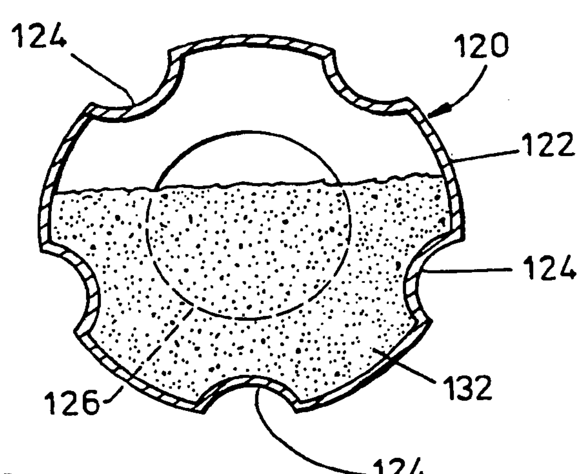

124
120
122
124
126
132
124

FIG. 7.

SPECIFICATION
Hydride Container

The present invention relates to the containment of gases such as hydrogen.

In recent years considerable attention has been given to the storage of hydrogen as the metallic hydride of various alloys or compounds. Metal hydrides can store large amounts of hydrogen at low, even sub-atmospheric pressures, in relatively small volumes and thus avoid the bulky storage containers necessitated by conventional hydrogen storage, e.g. as a gas in steel cylinders at high pressures or as a liquid at lower pressures in insulated containers. As well as requiring bulky containers, these means of containment are accompanied with the dangers of high pressure gas storage, or from leakage of gaseous hydrogen boiling-off from the liquid storage containers.

Hydridable metals are charged with gaseous hydrogen by introducing pressurised hydrogen into a valved container holding the hydridable metal wherein metal and hydrogen react exothermically to form a compound. The metal hydride is discharged when the valve of the container is opened whereby the endothermic decomposition of the hydride is accomplished. Normally the storage vessel is heated to increase the flow of hydrogen, or to provide the hydrogen at pressures greater than atmospheric. During the adsorption/desorption process the hydridable metal expands and contracts as much as 25% in volume as a result of hydrogen introduction and release from the metal lattice. Such dimensional change leads to fracture of the metal powder particles into fine particles. After several such cycles, the powder self-compacts causing inefficient hydrogen transfer. Additionally, and of even greater significance, high stresses due to the compaction of the powder and expansion during hydride formation are directed against the walls of the storage container. The stress within the powder has been observed to accumulate until the yield strength of the container is exceeded whereupon the container plastically deforms, buckles or bulges and eventually ruptures. Such rupture is extremely dangerous since a fine, pyrophoric powder is violently expelled by a pressurised, flammable hydrogen gas. Small, experimental cylinders have been found to burst when subjected to repetitive charging/discharging conditions.

Other gases can be stored as compounds formed by the reversible reaction between the gas and a solid, the reaction frequently accompanied by a volume change. For example ammonia can be stored as an ammine formed by its reversible reaction with certain metal halides. Such storage systems exhibit the same problems as described above for hydrides.

In the hydride systems, this being the area which has been most extensively researched, the expansion/compaction problem has been met by only partially filling the containers with hydridable metal powders. The problem of hydridable metal powder particle breakdown has been met in U.S. patent No. 4,036,944 by use of a thermoplastic elastomer binder to form pellets of the hydridable metal particles. Although this provides a solution to a portion of the problem of hydrogen storage, polymers are notoriously poor heat conductors and are subject to thermal deterioration. Since heat is generated during hydrogen charging and may be added during discharging, these polymer containing pellets are only useful under restrictive operational conditions. One further problem associated with hydridable metals is that it is important to ensure that it cannot react to any significant extent with atmospheric gases and moisture before it is loaded into pressure vessels.

The present invention is based on the discovery that gases of the type to which this invention relates can be stored more efficiently and safely in a valved metal vessel containing the solid with which the gas is to reversibly react in a plurality of metal sheathed storage containers.

According to the present invention a gas-containment system comprises a pressure resistant vessel having a valved port, a plurality of closed containers positioned within the vessel each container having a wall structure enclosing a definite volume, but deformable at pressures below the rupture pressure of the pressure-resistant vessel, where at least part of the wall structure is permeable to the gas to be contained and impermeable to solid particles; gas-absorbing particles located within the wall structure and occupying substantially less than the total volume of the container when in the gas-free state and not greater than the total volume of the container when in the gas-charged state, and the containers positioned such that there are a continuity of gas passages between and among the containers communicating with the valved port.

Because the individual containers are comparatively free to shift within the sealed pressure vessel, deformation of individual containers that may occur due to absorption and desorption of hydrogen will be accommodated by relative motion of the containers rather than be transmitted to the walls of the vessel. The voids between the containers provide passageways for hydrogen flow between the containers and the valve of the vessel.

Preferably the containers are made of metal and are of a generally cylindrical configuration and provided with one or more porous plugs. Advantageously the tubular container is fluted to provide more gas passages between the containers.

A preferred embodiment of the invention uses a container comprising a fluted tube section of generally circular cross section which is crimped closed at both ends over a gas-permeable filter disc. Within the closed tube section is a charge of the gas-absorbing particles. In the case of hydrogen storage, the hydridable metal occupies no more than about 78% of the volume of the tube section when the metal is in the hydrogen-free condition. The gas-permeable filter disc at

each end of the tube section has metal crimped over it only at its periphery, the crimped metal having generally radially-extending paths therein so as to provide means of gas passage in the event that one module presses tightly against another or against a flat surface.

Advantageously the container has a low ratio of length to diameter, for example, 1 to 10 and, preferably in the range 1 to 6. The ends of the container adjacent the filter discs are preferably of circular cross section with a diameter less than the diameter of the major portion of the tube section. The fluting along the main portion of the tube section is so constructed that the radius of curvature of the rounded grooves of the flutes is less than the radius of curvature of the tube section itself. This is to ensure the availability of gas passage space between undeformed tube sections even when tube section modules tend to nest with one another.

The invention will now be described by reference to the accompanying drawings in which:

Figure 1 is a schematic cross sectional view of a hydrogen storage container for use in gas-containment systems of the present invention;

Figure 2 is a schematic cross section of a further container having crimped ends;

Figure 3 is a schematic cross sectional view of a further embodiment of a container for use in the present invention and which excludes a threaded closure;

Figure 4 is a cross sectional view of the embodiment of Figure 3 on the line X—X;

Figure 5 is a schematic cross sectional view of a hydrogen storage unit in accordance with the present invention containing a plurality of hydrogen storage containers;

Figure 6 is an external view of the preferred embodiment of a container for use in the present invention and

Figure 7 is a cross sectional view of the container of Figure 6 on the line Y—Y.

Figure 1 shows in cross section a hydrogen storage container consisting of a tube 20 containing hydridable metal powder 22 which is retained within the tube by porous plugs 24 at both ends of the tube. The tube is normally a metal tube, this providing desirable heat transfer characteristics and thermal stability as well as strength and rigidity. The preferred metal is aluminium or copper although cheaper alternatives such as steel can also be used. The porous plug is one which allows the passage of hydrogen into and out of the container. It can consist of a porous metal filter or any other gas permeable but powder imp rmeable substance which exhibits sufficient thermal stability and inertness. Preferred materials are porous polymers, metal wools and felts. A pore size of less than about 5 microns is preferred for the porous plug. In Figure 1 the porous plug is shown to be held in place by crimping but it is also possible to use other fixing means, for example pr ss fitting, welding, brazing soldering and adhesive bonding. Clearly however the means of attachment must be thermally stable.

It has been found to be advantageous for the container to be of a generally cylindrical configuration to provide a rigid structure resistant to internal stress resulting from expansion of the hydridable metal which it contains. In addition, such a rigid structure is resistant to pressure as well as the expansion load transmitted from surrounding containers within a storage unit.

Figure 2 shows a further embodiment of a container comprising a tube 30, preferably of metal, containing hydridable metal powder 32, the powder maintained in the tube by a combination of a clamp 34 located in grooves 36, and by a gas permeable disc 38, normally of an inert fabric or felt material. The gas permeable disc 38 may be strengthened by a back-up screen 40. The far end of the container is crimped 42 to retain the hydridable powder within the tube.

Figure 3 shows a bullet shaped container which is generally cylindrical in configuration. The container is provided with concave flutes 51 along its walls, as is shown in Figure 4 which is a cross section on the line X—X. Hydridable metal powder 52 is retained within the container by threaded porous plug 54. The plug can be prepared from a porous metal or porous heat resistant polymer or any other inert, heat-resistant material that will retain the hydridable metal powder within the container yet allow ready passage of hydrogen gas into and out of the container means. The flutes 51 aid in providing hydrogen passages between the containers.

Figure 5 shows a hydrogen storage unit consisting of a sealed vessel 60 holding a plurality of storage capsules 62 with gas passageways 64 between them. These passages minimise the stress applied to the walls of the vessel. The vessel 60 is provided with valve means 66 allowing entry and exit of hydrogen gas to the vessel.

Figure 6 shows an external view of a container 120 consisting of a tube section 122 having a plurality of flutes 124 and reduced end sections 126. The end sections 126 are of circular cross section and are closed with gas-permeable plugs 128. The tube section is made of a heat conductive metal such as aluminium, copper or their alloys. The gas permeable plugs can be made of porous sintered metal such as aluminium, copper or nickel, the metal of the tube section 122 being crimped over the peripheries of the plugs 128 so that generally radially-extending gas passage channels exit in the crimped metal. When a plurality of these containers are used in a pr ssure r sistant vessel having a flat wall the gas channels 130 tend to ensure that hydrogen can flow to and from the porous plugs 128 even if the end of the container is forced against an abutting surface.

The container is shown as a cross section on the lines Y—Y in Figure 7, containing a hydrogen storage medium 132 in the hydrogen-charged condition. In this condition it is in the form of a

fine powder and has its greatest volume. Upon discharge the powder shrinks and occupies only about 60% of the internal volume of the container.

Suitable metals and metallic compounds for use in hydrogen storage units of the present invention include $CaNi_5$, $LaNi_5$, Mg_2Ni, V, and Mg. Although the preceding embodiments are all concerned with the storage of hydrogen, similar containers can be used in the storage of other gases which reversibly react with a solid, as has been explained earlier.

An example will now be described:

Aluminium containers of the configuration of that depicted in Figure 6, each of length 76.2 mm and outside diameter 12.2 mm, having an internal volume of 9 cc. were constructed and filled to achieve 40% voids in the hydride form, with a mischmetal/calcium/nickel alloy. In comparative tests, four of these filled containers containing 137 g of the alloy were used in a tubular hydrogen storage vessel close-fitting to the containers as opposed to the same amount of alloy being used in the same vessel but without any interior containment. In both instances vibration was applied to the pressure vessel to ensure initial maldistribution and subsequent packing and swelling of the hydridable metal. After two cycles of hydrogen charge-discharge, the vessel with no internal containment was visibly and dangerously bulged. The vessel having internal containment was unchanged in dimension after four hydrogen-charge-discharge cycles and gave all evidence of being capable of being used indefinitely.

Claims

1. A gas-containment system comprising a pressure resistant vessel having a valved port, a plurality of closed containers positioned within the vessel each container having a wall structure enclosing a definite volume, but deformable at pressures below the rupture pressure of the pressure-resistant vessel, where at least part of the wall structure is permeable to the gas to be contained and impermeable to solid particles; gas-absorbing particles located within the wall structure and occupying substantially less than the total volume of the container when in the gas-free state and not greater than the total volume of the container when in the gas-charged state, and the containers positioned such that there are a continuity of gas passages between and among the containers communicating with the valved port.

2. A system as claimed in claim 1 in which the containers are metal containers.

3. A system as claimed in claim 1 or claim 2 in which the gas is hydrogen and the gas-absorbing particles are of hydridable metal.

4. A system as claimed in any preceding claim in which the containers are of generally cylindrical shape.

5. A system as claimed in claim 4 in which the containers are fluted.

6. A system as claimed in any preceding claim in which the container comprises a fluted metal tube of low length to diameter ratio, crimped closed at each end over the periphery of a gas-permeable filter disc, the crimped metal having generally radially-extending paths therethrough, the container being filled to not greater than 78% of the volume of the container with hydridable metal in its hydrogen-free condition.

7. A system as claimed in claim 6 in which the ends of the tube section are circular and are of a reduced diameter from that of the fluted tube section.

8. A system as claimed in any preceding claim in which the gas permeable part of the wall structure or gas permeable filter disc is a disc of sintered metal.

9. A system as claimed in claim 6 in which the length to diameter ratio of the container is in the range 1 to 6.

10. A gas containment system suitable for the storage of hydrogen substantially as hereinbefore described having reference to any one of the Figures 1 to 7.

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